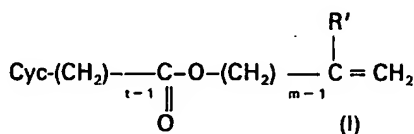


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(54) Copolymers of n-vinylpyrrolidone and a vinyl, allyl or methallyl ester of an  $\alpha$ - or  $\beta$ -cyclic carboxylic acid, and their use in cosmetics

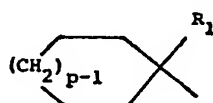
(57) Copolymers useful in hair lacquers and wave-setting lotions are derivable from the polymerisation of (a) N-vinylpyrrolidone and (b) an ester of an  $\alpha$ - or  $\beta$ -cyclic carboxylic acid, of the formula:



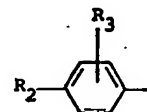
in which R' represents hydrogen or methyl, m is 1 or 2 and t is 1 or 2 such that if t = 1, Cyc represents:



(ii) a radical of the formula:

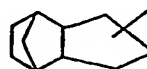


in which R<sub>1</sub> represents hydrogen or methyl and p is 1 or 2,  
 (iii) a radical of the formula:

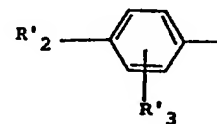


in which R<sub>2</sub> represents hydrogen, methyl, ethyl, tert.-butyl, ethoxy, butoxy or dodecoxy and R<sub>3</sub> represents hydrogen, C<sub>1-4</sub> alkyl or C<sub>1-4</sub> alkoxy, or

(iv) a radical of the formula:



and if t = 2, Cyc represents a radical of the formula:



in which R'<sub>2</sub> and R'<sub>3</sub> are as defined under R<sub>2</sub> and R<sub>3</sub>, respectively.

## SPECIFICATION

**Copolymers of n-vinylpyrrolidone and a vinyl, allyl or methallyl ester of an  $\alpha$ - or  $\beta$ -cyclic carboxylic acid, and their use in cosmetics**

5 The present invention relates to copolymers of N-vinylpyrrolidone and a vinyl, allyl or methallyl ester of an  $\alpha$ - or  $\beta$ -cyclic carboxylic acid; these copolymers can be used in cosmetics, in particular in lacquers and wavesetting lotions. 5

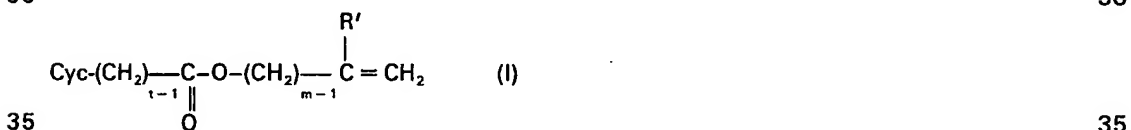
10 Polyvinylpyrrolidone (PVP), which forms a film which is both elastic and strong, has been widely used in cosmetic formulations such as lacquers and wavesetting lotions. 10

However, the use of polyvinylpyrrolidone has only proved totally satisfactory when the atmospheric humidity is relatively low. In fact, polyvinylpyrrolidone possesses a certain hygroscopicity, such that, after a certain time in a humid atmosphere, the polyvinylpyrrolidone film tends to become sticky. To overcome the hygroscopicity of polyvinylpyrrolidone, it has been 15 proposed to use copolymers of N-vinylpyrrolidone and vinyl acetate. These copolymers are less sensitive to atmospheric humidity and furthermore possess good fixing properties. By varying the proportion of vinyl acetate, it is possible to influence some of the properties of the film, in particular the hardness and the hygroscopicity. 15

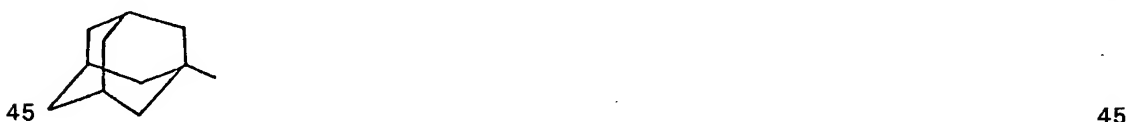
However, these copolymers of N-vinylpyrrolidone and vinyl acetate do not always possess a very good lacquering ability and can be relatively brittle. 20

The present invention is intended to overcome the disadvantages of the films produced from N-vinylpyrrolidone, by providing copolymers obtained by polymerising N-vinylpyrrolidone with at least one vinyl, allyl or methallyl ester of an  $\alpha$ - or  $\beta$ -cyclic carboxylic acid. In fact, it has been found that by polymerising N-vinylpyrrolidone with this type of ester, the copolymers obtained 25 possess excellent properties, in particular cosmetic properties, that is to say moderate hardness, very low hygroscopicity, good lacquering ability and a pleasant feel. 25

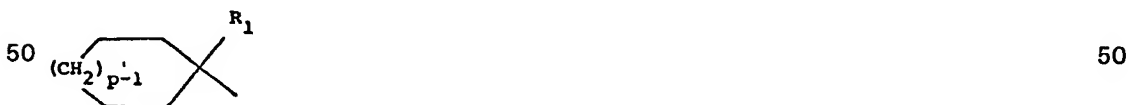
The present invention provides polymers which contain units resulting from the polymerisation of (a) N-vinylpyrrolidone with (b) at least one vinyl, allyl or methallyl ester of an  $\alpha$ - or  $\beta$ -cyclic carboxylic acid, corresponding to the following formula: 30



(i) a radical of the formula: 40



(ii) a radical of the formula:



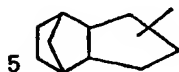
in which R<sub>1</sub> represents a hydrogen atom or a methyl radical and p is 1 or 2,

(iii) a radical of the formula: 55



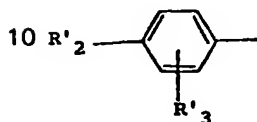
in which R<sub>2</sub> represents a hydrogen atom or a methyl, ethyl, tert.-butyl, ethoxy, butoxy or dodecoxy radical and R<sub>3</sub> represents a hydrogen atom, an alkyl radical having 1 to 4 carbon atoms or an alkoxy radical having 1 to 4 carbon atoms, or 65

(iv) a radical of the formula:



5

and if  $t = 2$ , Cyc represents a radical of the formula:



10

15 in which  $R'_2$  and  $R'_3$  are as defined under  $R_2$  and  $R_3$ , respectively.

15

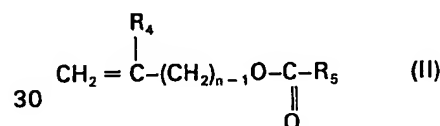
Amongst the vinyl, allyl or methallyl esters of the formula (I), the following may be mentioned in particular: the vinyl, allyl and methallyl esters of adamantane-1-carboxylic acid, cyclohexane-carboxylic acid, cyclopentane-carboxylic acid, benzoic acid, phenylacetic acid, 4-tert.-butylbenzoic acid, 1-methylcyclopentane-1-carboxylic acid, 1-methylcyclohexane-1-carboxylic acid, tricyclo[5.2.1.0.2,6]-decane-3-carboxylic acid and tricyclo[5.2.1.0.2,6]-decane-4-carboxylic acid, these last two acids being sold, in the form of a mixture, by HOECHST, under the tradename TCD Carboxylic Acid S.

20

The copolymers according to the invention can also contain units of at least one other monomer which is:

25 1. A vinyl, allyl or methallyl ester of the formula:

25



30

in which  $n$  is 1 or 2,  $R_4$  represents a hydrogen atom or a methyl radical and  $R_5$  represents a linear or branched alkyl radical having from 1 to 21 carbon atoms.

35 Amongst the esters of the formula (II), the following may be mentioned in particular: the vinyl, allyl and methallyl esters of acetic acid, propionic acid, butyric acid, pivalic acid, hexanoic acid, octanoic acid, decanoic acid, lauric acid, myristic acid, palmitic acid, stearic acid, isostearic acid, behenic acid, 2-ethyl-hexanoic acid, 2,2-dimethylpentanoic acid, 2,2-dimethyl-hexanoic acid, 2,2-dimethyloctanoic acid, 2,2-dimethyl-decanoic acid, 2,2,4,4-tetramethylvaleric acid, 2-isopropyl-2,3-dimethylbutyric acid, 2-methyl-2-ethylheptanoic acid, 2-methyl-2-propylhexanoic acid, 2-methyl-2-isopropylhexanoic acid, 3,5,5-trimethylhexanoic acid and their isomers, and also mixtures thereof and in particular the mixture sold by SHELL under the tradename "Versatic Acid" and the mixtures sold by UGINE-KUHLMANN under the tradenames "CEKANOIC  $C_8$ ,  $C_9$  and  $C_{10}$  Acids".

40

45 2. A vinyl ether of the formula:

45

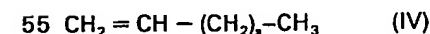


in which  $R_6$  represents a linear or branched alkyl radical having from 6 to 18 carbon atoms.

50 Amongst the vinyl ethers of the formula III, the following may be mentioned: hexyl vinyl ether, octyl vinyl ether, decyl vinyl ether, dodecyl vinyl ether, hexadecyl vinyl ether and octadecyl vinyl ether. or

50

3. An  $\alpha$ -olefine of the formula:



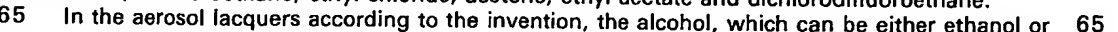
55

in which  $s$  is an integer from 3 to 15.

Amongst the  $\alpha$ -olefines of the formula IV, the following may be mentioned: hex-1-ene, oct-1-ene, dec-1-ene, dodec-1-ene and octadec-1-ene.

60 The copolymers according to the invention can generally be represented as having recurring units of the following general formula:

60



isopropanol, is generally present in an amount of 5 to 80%, and preferably 6 to 70%, by weight.

Propellants which can be used in particular for the aerosol lacquers are fluorochlorinated hydrocarbons, either used singly or as a mixture, especially those known under the tradenames "Freon" and in particular "Freons 11, 12, 22, 133A and 142b".

Propellants which can also be used are carbon dioxide, nitrous oxide ( $N_2O$ ), dimethyl ether and hydrocarbons such as propane, butane and isobutane, these propellants being used either singly or as a mixture with one another or with one or more "Freons".

When the compositions are in the form of shampoos, they contain, in addition to the polymer according to the invention, at least one anionic, cationic or non-ionic surface-active agent.

The compositions according to the invention can also contain various ingredients which are generally used in this type of composition, such as plasticisers, agents for imparting gloss, perfumes, dyestuffs and restructuring agents.

The following examples further illustrate the present invention:—

#### PREPARATION EXAMPLES

##### EXAMPLE 1

A solution of 35 g of vinyl 4-tert.-butyl-benzoate, 35 g of vinyl acetate, 30 g of N-vinylpyrrolidone and 0.2 g of azo-bis-isobutyronitrile in 300 g of ethanol is introduced into a round-bottomed flask equipped with a condenser, a mechanical stirrer and a nitrogen inlet.

The mixture is subsequently heated under reflux for 24 hours, whilst stirring, and the polymer is then precipitated in ethyl ether. After filtration, the polymer is dried at 50°C under reduced pressure.

The yield is 42% and the polymer obtained has a viscosity of 1.56 cP, measured in a 5% strength solution in dimethylformamide (DMF) at 34.6°C.

##### EXAMPLE 2

30 g of N-vinylpyrrolidone, 15 g of vinyl cyclohexanoate, 55 g of vinyl acetate, 0.5 g of tert.-butyl 2-ethylperhexanoate and 25 g of ethanol are introduced into a round-bottomed flask equipped with a condenser, a mechanical stirrer and a nitrogen inlet.

The mixture is subsequently heated under reflux for 24 hours, whilst stirring, and then, when the polymerisation reaction is complete, the polymer is precipitated in ethyl ether.

After filtration, the polymer is dried at 50°C under reduced pressure.

The yield is 80% and the polymer obtained has a viscosity of 2.4 cP, measured in a 5% strength solution in dimethylformamide (DMF) at 34.6°C.

The copolymers in Table I were also prepared in accordance with the procedures described in Example 1 and 2 above:

TABLE 1

Monomer % by weight	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9	Example 10	Example 11	Example 12	Example 13	Example 14
N-vinylpyrrolidone	70	50	30	70	50	40	30	35	40	40	30	35
vinyl 4-tert.-butyl- benzoate	30	50	70	15	25							
allyl 4-tert.-butyl- benzoate				10						5		
vinyl benzoate							15					12
vinyl cyclopentanolate								15	5		15	
vinyl phenylacetate									10	10		
allyl benzoate												
vinyl acetate				15	25	50	50	45	10	40	50	38
vinyl propionate									45			10
allyl propionate										5		5
allyl stearate							5					
octadecyl vinyl ether											5	
dodecyl vinyl ether								5				
Yield %	80	62	26	73.2	70	40	42	55	48	59	92	64
Viscosity (5% strength solution in DMF at 34.6°C)	2.05	1.89	1.67	1.88	1.54	1.52	1.82	1.69	1.54	1.68	2.3	1.73

\*obtained in accordance with the process of Example 1

\*\*obtained in accordance with the process of Example 2

**COMPOSITION EXAMPLES****EXAMPLE A**

An aerosol lacquer is prepared according to the invention by packaging the following ingredients in a container:

5				
	Copolymer prepared in accordance with Example 1	3 g		5
	Ethanol (or isopropanol)	40 g		
	Methylene chloride	20 g		
10	Propellant: mixture of 35% of propane and 65% of butane	40 g		10

In this example, the copolymer prepared in accordance with Example 1 can be replaced by the same amount of the copolymer prepared in accordance with Example 4.

**15 EXAMPLE B**

An aerosol lacquer is prepared according to the invention by mixing the following ingredients:

	Copolymer prepared in accordance with Example 3	3 g		
	Ethanol	60 g		
20	Propellant: mixture of 35% of propane and 65% of butane	40 g		20

**EXAMPLE C**

An aerosol lacquer is prepared according to the invention by mixing the following ingredients:

25				25
	Copolymer prepared in accordance with Example 2	7.6 g		
	Ethanol q.s.p.	100 g		

22 g of the composition thus obtained are then packaged in an aerosol container together with 78 g of a 61.5/38.5 mixture of Freon 11 and Freon 12.

When this lacquer is applied to the hair, no powder formation is observed with time and the hair does not become sticky, even in a humid atmosphere.

**EXAMPLE D**

35 A wavesetting lotion is prepared according to the invention by mixing the following ingredients:

	Polymer prepared in accordance with Example 4	2 g		
	Perfume	0.15 g		
40	Ethanol	46 g		40
	Water q.s.p.	100 g		

In this example, the polymer prepared in accordance with Example 4 can advantageously be replaced by the same amount of one of the polymers prepared in accordance with Examples 5 to 8 or 14.

After this wavesetting lotion has been applied to the hair, the latter is wound onto wavesetting rollers and then dried. The waveset holds very well with time and there is no powder formation.

**EXAMPLE E**

50 A wavesetting lotion is prepared according to the invention by mixing the following ingredients:

	Copolymer prepared in accordance with Example 9	3.5 g		
	Perfume	0.2 g		
55	Sufficient dyestuff to colour the lotion	0.15 g		55
	Isopropyl alcohol	50 g		
	Water q.s.p.	100 g		

When applied in the conventional manner, this wave setting lotion makes it possible to impart, to the hair, a glossy appearance and an excellent hold with time.

In this example, the polymer prepared in accordance with Example 9 can advantageously be replaced by the same amount of one of the polymers prepared in accordance with Examples 10 to 12.

**65 EXAMPLE F**

A rinsing product or "rinse", in the form of an emulsion, is prepared according to the invention by mixing the following ingredients:

	Liquid petrolatum	9.6 g	
5	Polyglycerolated fatty alcohols (C <sub>16</sub> C <sub>18</sub> ) (containing 2 to 6 mols of glycerol)	6.5 g	5
	Polymer prepared in accordance with Example 13	1.5 g	
	Water q.s.p.	100 g	

- 10 This product is applied to hair which has been washed and towel-dried, by spreading it carefully over the whole head of hair. After a few minutes have elapsed, the hair is carefully rinsed. 10

The hair is glossy and easy to comb out.

- 15 In this example, the polymer according to Example 13 can advantageously be replaced by the same amount of one of the polymers prepared in accordance with Examples 2 to 5 and 8. 15

#### EXAMPLE G

An ionic shampoo is prepared according to the invention by mixing the following ingredients:

20	Triethanolamine lauryl-/myristyl-sulphate	12 g	20
	Copra diethanolamide	2 g	
	Myristyldimethylamine oxide	1.5 g	
	Copolymer prepared in accordance with Example 10	1.5 g	
	Lactic acid q.s.p. pH = 6.5		
25	Water q.s.p.	100 g	25

#### EXAMPLE H

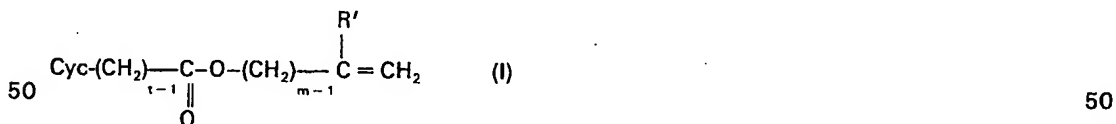
A cationic shampoo is prepared according to the invention by mixing the following ingredients:

30	Cetyltrimethylammonium bromide	2 g	30
	Polyglycerolated lauryl alcohol containing 4 mols of glycerol	12 g	
	Polymer prepared in accordance with Example 6	1 g	
35	Perfume	0.2 g	35
	Lactic acid q.s.p. pH = 4.5		
	Water q.s.p.	100 g	

- 40 In this example, the polymer prepared in accordance with Example 6 can advantageously be replaced by the same amount of one of the polymers prepared in accordance with Examples 7 or 13. 40

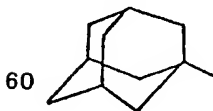
#### CLAIMS

1. A copolymer derivable from the polymerisation of (a) N-vinylpyrrolidone and (b) at least one vinyl, allyl or methallyl ester of an  $\alpha$ - or  $\beta$ -cyclic carboxylic acid of the formula: 45



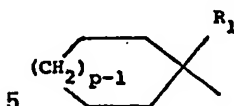
in which R' represents a hydrogen atom or a methyl radical, m is 1 or 2 and t is 1 or 2 such that if t = 1, Cyc represents:

- 55 (i) a radical of the formula: 55



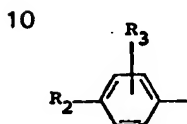
(ii) a radical of the formula:





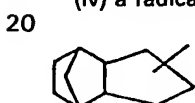
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in which R<sub>1</sub> represents a hydrogen atom or a methyl radical and p is 1 or 2,  
(iii) a radical of the formula:



10

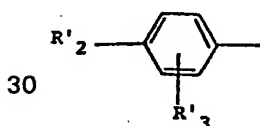
15 in which R<sub>2</sub> represents a hydrogen atom or a methyl, ethyl, tert.-butyl, ethoxy, butoxy or dodecoxy radical and R<sub>3</sub> represents a hydrogen atom, an alkyl radical having 1 to 4 carbon atoms or an alkoxy radical having 1 to 4 carbon atoms, or  
(iv) a radical of the formula:



20

25 and if t = 2, Cyc represents a radical of the formula:

25



30

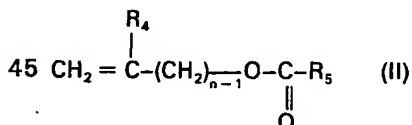
in which R'<sub>2</sub> and R'<sub>3</sub> are as defined under R<sub>2</sub> and R<sub>3</sub> respectively.

2. A copolymer according to claim 1, in which the said ester is a vinyl, allyl or methallyl ester of adamantane-1-carboxylic acid, cyclohexanecarboxylic acid, cyclopentane-carboxylic acid, 35 benzoic acid, phenylacetic acid, 4-tert.-butylbenzoic acid, 1-methylcyclopentane-1-carboxylic acid, 1-methylcyclohexane-1-carboxylic acid, tricyclo[5.2.1.0.<sup>2,6</sup>]decane-3-carboxylic acid or tri-cyclo[5.2.1.0.<sup>2,6</sup>]decane-4-carboxylic acid.

3. A copolymer according to Claim 1 or 2 which is also derivable from at least one other  
40 monomer which is:

40

(i) a vinyl, allyl or methallyl ester of the formula:



45

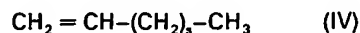
in which n is 1 or 2, R<sub>4</sub> represents a hydrogen atom or a methyl radical and R<sub>5</sub> represents a  
50 linear or branched alkyl radical having from 1 to 21 carbon atoms,  
(ii) a vinyl ether of the formula:

50



55 in which R<sub>6</sub> represents a linear or branched alkyl radical having from 6 to 18 carbon atoms, or  
(iii) an α-olefine of the formula:

55



60 in which s is an integer from 3 to 15.

60

4. A copolymer according to any one of the preceding claims, which comprises units of the following formulae



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**.30**

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